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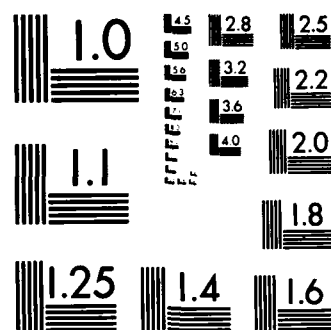# CHEMILUMINESCENCE AND LASER INDUCED
FLUORESCENCE OF BORON ATOM REACTIONS.

Principal Investigator: Paul Davidovits

Grant No: AFOSR 80-0061

Final Progress Report: June 30, 1983.

Summary

The purpose of the work sponsored by grant AFOSR 80-0061 was to study the highly exoergic gas phase reactions of boron atoms. The main goal of these studies is to obtain a basic understanding of exoergic reactions of non metal atoms. These types of reactions play a fundamental role in fields such as combustion, plasma chemistry, laser induced chemistry and chemical lasers.

We have completed rate and chemiluminescence studies of boron atom reactions with most of the important oxygen containing molecules of interest. From the results of these studies we are now able to suggest a qualitative model that may explain the nature of these reactions.

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The purpose of this effort was to study the highly exoergic gas phase reactions of boron atoms. The main goal of these studies was to obtain a basic understanding of exoergic reactions of non-metal atoms which play a fundamental role in fields such as combustion, plasma chemistry, laser induced chemistry and chemical lasers. The kinetic and chemiluminescence studies of boron atom reactions with most of the important oxygen containing molecules of interest were completed. Semi-empirical theoretical studies were carried out to help understand the observed reactivities. A qualitative model was developed which predicts that reactivity depends on the following three factors: the local electron affinity, the ionization potential of the atom, and the electron density at the reactive site. Twelve papers have been or are in the process of being published as a result of this work.

1. METHOD AND PURPOSE OF EXPERIMENTS

We have developed experimental techniques for studying boron atom reactions.

(a) **Total Reaction Rate Studies:** A flow apparatus was built to measure the total cross section for the reaction of boron atoms with a wide range of reactive molecules.

A schematic diagram of the flow tube apparatus is shown in Fig. 1. The quartz flow tube (3.5 cm diameter, 140 cm length) was evacuated by a high speed rotary pump. Boron atoms were produced in a microwave discharge of a 0.02% mixture of diborane in argon. The boron density in the reaction zone was about 10^{10} atoms x cm^{-3}. Reactant gases were introduced through a multiholed Teflon loop and their flow rates were measured using calibrated rotameters. The total pressure in the reaction zone was measured on a Wallace and Tiernan gauge.

Fig. 1

Boron atoms were detected by absorption of 2497 Å resonance light obtained from a neon-filled boron hollow cathode lamp. The transmitted light was detected using a monochromator, photomultiplier combination. The quartz optical windows were buffered by a small flow of argon which was shown not to affect the kinetics. The entire optical system was mounted on a movable platform so that absorption measurements could be made as a function of distance from the stationary inlet. Typical rate data for the B + O_2 reaction are shown in Figure 2.
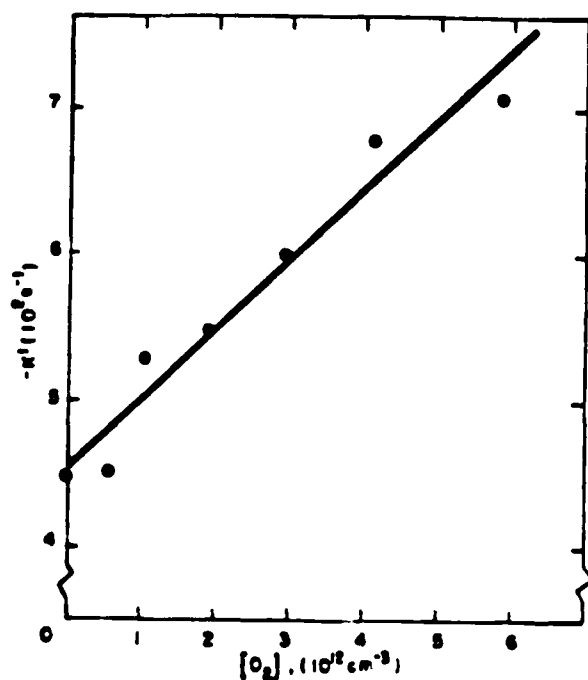

Fig.   2

(b) **Chemiluminescence Studies:** Many of the reactions under study are sufficiently exoergic to produce electronically excited product molecules. A single collision beam apparatus was constructed to study electronically excited molecules produced in the boron atom reactions.

A simplified sketch of the beam apparatus is shown in Figure 3. It consists of two 18 inch stainless steel chambers pumped by a 10 inch diffusion pump. The various gauges, light baffles, heat shields and shutters are not shown. The crucible which contains solid boron was heated by electron bombardment. Crucibles are machined from tantalum or from tungsten and are lined with a carbon liner. The material can be heated up to about $2500^{\circ}C$. The method of introduction of the reactant molecules depends on the reaction to be studied.

The chemiluminescence from the reaction zone is detected by a spectrometer-photomultiplier-photon counter combination. The photon counter is manufactured by Ortec. The photomultiplier is cryogenically cooled. An elaborate light shielding arrangement blocks the stray light from the thermally heated components and allows the detection of signals as low as five counts per second. The detection apparatus is calibrated to measure absolute photon yields.

Figure 4 shows a typical spectrum of the chemiluminescence observed in the $B + O_2$ reaction. This is radiation from $A^2\pi \rightarrow X^2\Sigma^+$ transition of BO, plotted from the analogue output of the photon counter.

These experiments allowed us to measure absolute cross sections for the production of electronically excited states and the vibrational population distribution in those states.
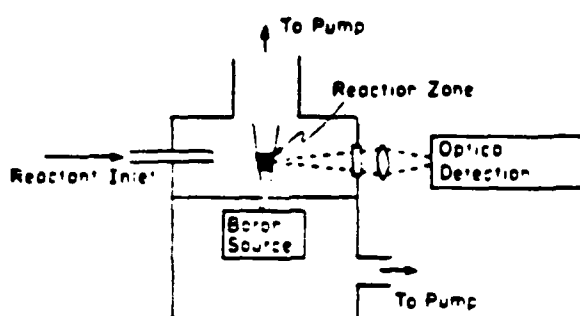
Fig. 3

Schematic diagram of the apparatus

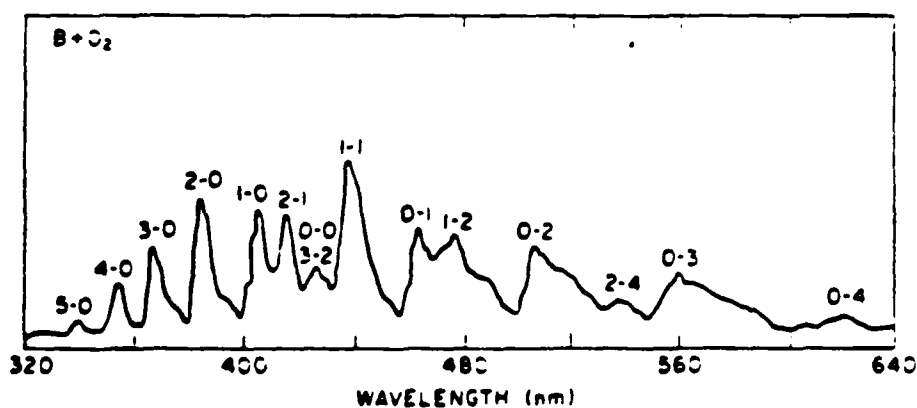
Fig. 4

Chemiluminescence spectrum observed in the B + O₂ reaction

(c) **LIF Vibrational Excitation Studies.** The distribution of vibrational excitation in product molecules provides information about the reaction complex. We have such information about the electronically excited molecules from the chemiluminescence studies. Similar information about the ground state products would be useful. For certain types of simple molecules laser-induced fluorescence (LIF) is the most effective method of detection and analysis of ground state vibrational distributions (24). Most of the molecules listed in Table VII fall in this category. These molecules are well characterized and have band systems in the spectral region suitable for LIF studies.

We have obtained a dye laser system and have built a new flow apparatus coupled to this laser. We have obtained preliminary LIF spectra from the reaction of B + O_2. This work is still in progress.

2. RESULTS

We have completed the studies of boron atom reactions with a large number of oxygen containing molecules. These reactants can be grouped in the following categories.

a) Simple molecules; O_2, SO_2, N_2O, CO_2, H_2O, H_2O_2, NO_2, OCS, CS_2

b) Alcohols: Methanol, Ethanol, n-propyl alcohol, isopropyl alcohol, allyl alcohol

c) Thiols: n-propane thiol

d) Heterocyclic Compounds: Oxetane, Furan, 2,5-dihydrofuran, tetrahydrofuran, dioxane, thiophene

e) Ethers: diethyl ether

f) Episulfide: Propylene Sulfide

g) Epoxides: Ethylene oxide, Propylene Oxide, 1,2-Butylene Oxide, Cyclopentene Oxide, Cyclohexene Oxide, Styrene Oxide, Butadiene monoxide, 1,2-,3,4 diepoxy butane, 3-vinyl-7-oxabicyclo (4.1.0) heptane.

h) Halogenated Epoxides: Epifluorohydrin, Epichlorohydrin, Epibromohydrin, 3,3, 3 trichloro-1,2 epoxypropane

i) Halogenated Alcohols: 1,1,1-trichloro-2-propanol, 1-chloro-2-propanol.

This work has yielded many interesting results, most of which have been discussed in journal articles listed in the publication section of this report.

For the sake of conciseness, we will not present all of this work in the present report. Here we will focus primarily on a salient set of results which led us to formulate a qualitative model for these reactions.

In Table I we list total reaction cross sections (σ_T) and chemiluminescence cross sections (σ^*) for several simple oxygen containing molecules. The total reaction cross sections are obtained from the flow tube rate measurements and the cross sections for the production of electronically excited states are measured in the beam experiments. The chemiluminescence experiments distinguish between electronically excited BO and BO_2 products. In the B + SO_2 reaction excited states of both BO and BO_2 were observed. For future discussion the table also

shows the electron affinity of the reactant molecule. In Table II we show the cross sections for the reaction of boron with a sequence of epoxides.

For the purposes of the present discussion we will note the following features in these data:

Perhaps the most striking feature of the results in Table I is the low reactivity of boron with N_2O and CO_2. Whereas the reaction cross sections for O_2, SO_2 and NO_2 are close to gas kinetic, the reactivities of N_2O and CO_2 are about a thousand times lower.

In the reaction of boron with SO_2 both BO and BO_2 are formed. In the reaction with NO_2 there is no evidence for BO_2 formation.

In Table II we observe that reaction rates for epoxypropane and epoxybutane are nearly identical. This is expected if one assumes that the boron interacts only with the reactive oxygen site. The magnitude of these cross sections is about the same as the geometric size of the epoxide ring which indicates that the reactions of boron with propylene and butylene oxides are not hindered by an activation energy.

Since diepoxybutane contains two reactive sites, as a first guess, one would expect its reaction cross section to be twice that of epoxypropane or epoxybutane. In fact, the measured cross section is actually about 30% smaller. Reductions in the reaction rate are also observed in the chlorinated epoxides. Most notably, the reaction rate with the trichloro expoxypropane
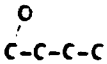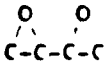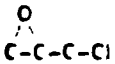
Tables I and II
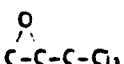
REACTION CROSS SECTIONS

Table I	σ_T TOTAL REACTION CROSS SECTION (A^2)		σ^* CHEMILUMINESCENT CROSS SECTION (A^2)	
$B + O_2$	5.2	$BO(A^2\pi) + O(^3P_2)$	0.048	
$B + SO_2$	13	$BO(A^2\pi) + SO(X^3\Sigma^-)$	0.004	
		$BO_2(A^2\pi) + S(^3P_2)$	0.0038	
$B + N_2O$	0.0024	$BO(A^2\pi) + N_2(X^1\Sigma_G)$	.01	
$B + NO_2$	$(20)^*$	$BO(A^2\pi) + NO(X^2\pi)$	0.23	
$B + CO_2$	0.0082	$BO(X^2\Sigma^+) + CO(X^1\Sigma_G^+)$	0	

NOTE: CROSS SECTION   DEFINED AS $\sigma = \dfrac{\text{RATE CONSTANT}}{\text{COLLISION VELOCITY}}$

* ESTIMATE

Rates and cross sections for the reaction of boron with the epoxides

Reactant	Structure	k_2 (cm^3 molecule^{-1} s^{-1})	σ (A^2)	σ^* (A^2)
C_3H_6O 1,2-epoxypropane	O /\ C-C-C	8.6×10^{-11}	1?	0.0067
C_4H_8O 1,2-epoxybutane	O /\ C-C-C-C	8.8×10^{-11}	11	0.0045
$C_4H_6O_2$ 1,2,3,4-diepoxybutane	O O /\ /\ C-C-C-C	5.5×10^{-11}	6?	0.010
C_3H_5ClO 1-chloro-2,3-epoxypropane	O /\ C-C-C-Cl	5.7×10^{-11}	7.1	0.0024
$C_3H_3Cl_3O$ 1,2-epoxy-3,3,3-trichloropropane	O /\ C-C-C-Cl$_3$	1.5×10^{-11}	1.9	0.0005

is reduced by a factor of five. The reduction in the reaction rate of boron with the epoxide ring may be even greater since here we cannot separate the possible reactions of boron with chlorine from those with oxygen. Similar reductions were observed in the chemiluminescent cross sections measured in single-collision beam experiments.

3. DISCUSSION OF RESULTS:

We will discuss two aspects of our work (i) the vibrational distribution in the electronically excited BO product molecule and (ii) the observed reactivities.

(i) Vibrational Distributions.

A detailed statistical analysis of the vibrational distribution shows that the results are best fitted by a statistical model which assumes that only those vibrational modes of the polyatomic product are excited which correspond to the conformation change from reactant to product.

(ii) Reactivity.

In the past several factors have been suggested as playing a key role in determining reactivity. Among the most commonly invoked are the exoergicity of the reaction, spin conservation, electron shell configuration and various correlation rules. We have examined these factors in detail and have shown that they cannot explain the low reactivity of boron with CO_2 and N_2O. (Due to space limitation we cannot present this discussion here).

These commonly used factors also fail to provide a consistent explanation for the observed reactivities of other elements. This is illustrated in Table III which shows the measured rates for the highly exoergic reactions of the group IV elements (C, Si, Ge, Sn, Pb) with O_2 and N_2O.

GROUP IV. REACTION CROSS SECTIONS ($Å^2$)

ELEMENT	O_2	N_2O	
C	6	3	TABLE III
Si	60	47	
Ge	30	1.5	
Sn	5	0.0016	
Pb		<0.0005	
B	5.2	0.0024	

The Rate Coefficients for the reaction in TABLE III have been measured by several groups. The Rate Coefficients quoted by different sources vary at times by as much as an order of magnitude. However, the basic observation on the grouping of reactivities discussed in the text emerges in all the measurements. For clarity of presentation, we have quoted only one cross-section for each reaction and we have omitted the error limits.

Here the remarkable feature in the measured reaction rates of N_2O is the sharp decrease in the reactivity of Sn and Pb compared to C, Si, and Ge. The reactivity of the latter grouping is more than three orders of magnitude higher. Why is the reaction rate of N_2O so much higher with carbon and silicon than with boron, tin and lead? Again, the usual arguments including the application of various correlation rules do not

provide a consistent explanation of the observed results.

Since the usual approaches did not explain the experimental results, we examir d the process from another point of view. The experimental results are explained qualitatively by a model which uses the basic ideas of the frontier-orbital theory and considers the local electron distribution within the reacting system. While this model is only qualitative, it has the potential for quantitative formulation. Because of space restrictions, the model and its predictions will be presented only in brief outline.

4. THE REACTION MODEL

(i) **The Role of Electron Affinity in the Entrance Channel** In order for a reaction to occur there must be a movement of electrons in the reaction complex. Only through this process can old bonds be broken and new bonds be formed. This is consistent with the frontier orbital theory of reactions where the electron which initiates the reaction flows from the highest occupied molecular orbital (HOMO) of one species to the lowest unoccupied molecular orbital (LUMO) of the other. In most boron atom reactions the initiating movement of electrons is expected to be from the boron to the reactive site in the molecule.

In such a reaction process where an electron begins to flow from one species to the other, one expects that the electron affinity will play a role in determining reactivity. A negative electron affinity at the oxygen end of the reactant molecule

would block the initial flow of electrons and thus hinder the reaction. Of course, the electron affinity which affects the reactivity would be that within the collision complex rather than the electron affinity of the isolated molecule. This hypothesis would lead one to expect that reactions with molecules having large negative electron affinities would be blocked while the reactions of molecules with large positive electron affinities would proceed with gas kinetic cross sections. The reactivities of molecules with small electron affinities (positive or negative) may fall into either category, depending on the interactions within the complex. The results in Table I provide support for this point of view. It is evident that NO_2, SO_2 and O_2 which have large positive electron affinities react with gas kinetic cross sections while the reactivities of CO_2 and N_2O which have low or negative electron affinities are greatly hindered.

This model can also explain qualitatively why BO_2 is formed in the $B-SO_2$ reaction but not in the $B-NO_2$ reaction. If we assume that within the collision complex BO is formed first, the formation of BO_2 is then perhaps governed by the electron affinity of the other component. (That is, SO in the reaction with SO_2 and NO in the reaction with NO_2.) Our experimental results are consistent with this suggestion. The electron affinity of SO is quoted to be 1.02 eV. Thus one would anticipate the formation of BO_2 in the reaction of boron with SO_2. On the other hand the vertical electron affinity of NO is

close to zero (32) and therefore in the reaction with NO_2 the BO_2 channel is blocked.

It should be noted that in the "harpoon" model which governs the reaction of metal atoms, the process is likewise initiated by electron transfer. The interactions of non-metals however, are expected to be both qualitatively and quantitatively different. In metal atom reactions the internuclear distance at the point of electron transfer is greater than 5Å. At this range, covalent interactions are very small. For the reactions with boron the internuclear distance of the crossing between the covalent and ionic curves where the electron jump may occur is calculated to be less than 2Å. At such small internuclear distances interactions are more complex. The distribution of electrons within the reactant molecule is significant.

This point of view can explain the reactive behavior of N_2O. The N_2O molecule has a negative overall electron affinity. However, as has been shown by our MNDO computer calculations, only the oxygen end of the molecule opposes the approach of the electron. An electron can flow freely toward the nitrogens in the molecule. The model suggests that if the pathway to the formation of the nitride is energetically accessible, the reaction will proceed readily. This is the case for carbon and silicon. The large cross sections which are observed only for C and Si may be due to the reactions with the nitrogen end of the molecule rather than the oxygen. In reactions with B, Sn and Pb

energetics allow only the formation of the oxide. Since the oxygen end of the molecule repels the initiating electron flow, these reactions are hindered.

(ii) **Exit Channel.**

Even if the reaction is not hindered in the entrance channel a barrier may still be present in the exit channel. As an example, an exit channel barrier may arise in the following way. After the electron flows from the atom to the molecule, a second step is required to complete the reaction. Since the product molecule (for example BO or BF) is predominantly covalent, a reverse electron flow must occur to complete the reaction. If this retroflow is hindered, the reactivity is lowered. As is discussed in the following section the reduced reactivity of the chlorinated epoxides is due to yet another type of an exit barrier.

5. COMPUTER STUDIES

The model as we have described it, predicts that reactivity depends on the following three factors: (i) The "local electron affinity", a negative electron affinity at the reactive site will block reactions. (ii) Ionization potential of the atom. A high ionization potential may block the electron flow which initiates the reaction. (iii) The electron density at the reactive site of the molecule. A lowered electron density at the reactive site may reduce reactivity by hindering the retro-flow of electrons necessary to complete the covalent

bonds. The aim of our theoretical work is to study these parameters quantitatively and to develop expressions which predict reactivities in terms of these and other variables which may be revealed in the course of our work.

Initial theoretical work was done with MNDO computer programs designed to calculate electron densities and molecular structure. With these programs we calculated the potential energy of an atom at various sites in the neighborhood of the reactant molecules. The energies were calculated as a function of various parameters of interest.

Our preliminary calculations are in qualitative agreement with the model described in the previous section. As an example of the type of results obtained we present here a sketch of the potential energy for the coordinates describing the reactions of boron with the epoxides C_3H_6O and $C_3H_3Cl_3O$. For simplicity, energies and bond lengths have been omitted from the drawings.

As can be seen the B + C_3H_6O proceeds smoothly to completion. However, in the reaction of boron with the chlorinated epoxide an additional complex can be formed which blocks the BO exit channel. This may be the cause of the reduced reactivity observed for this molecule. [See Fig. 5]
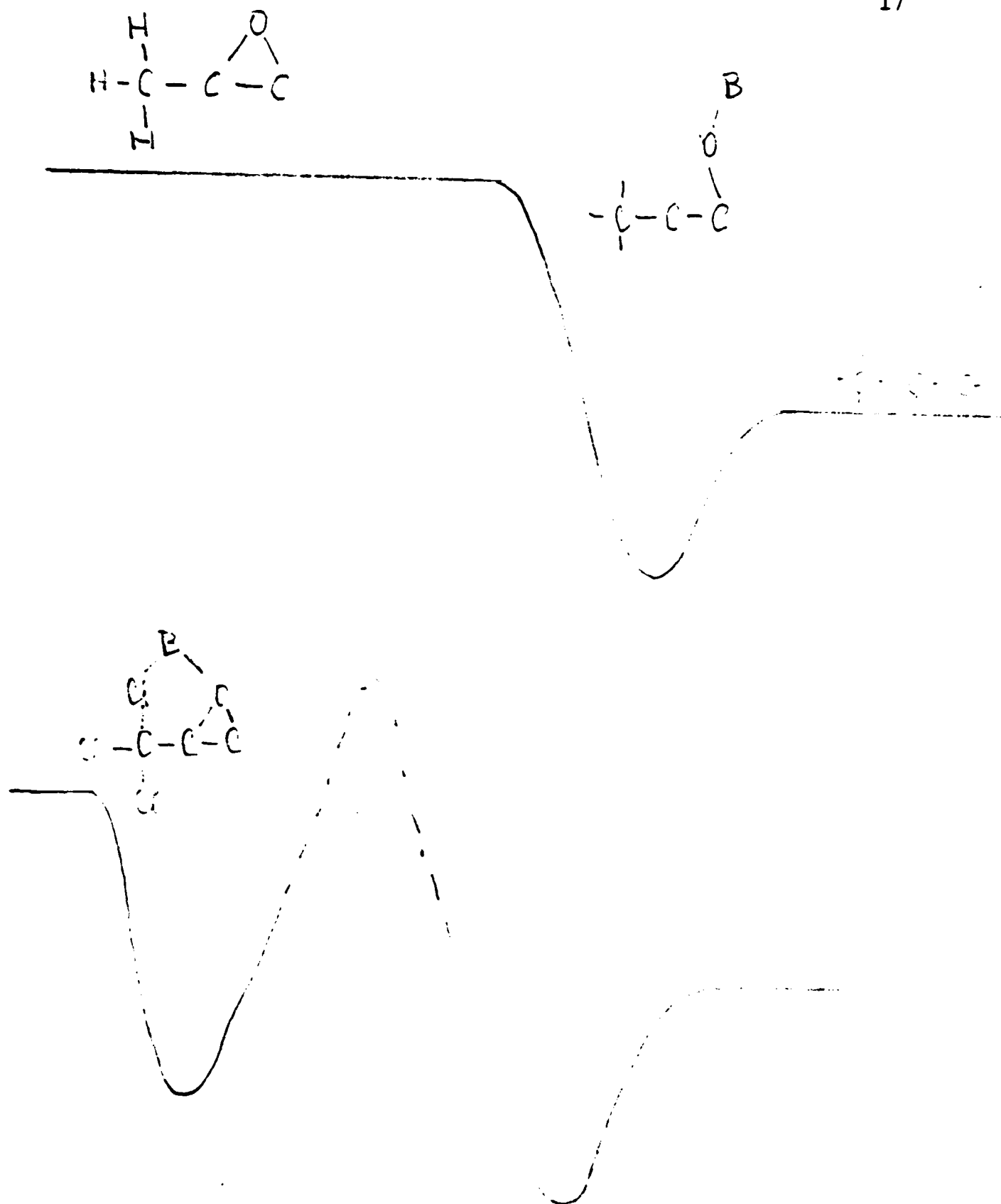
Fig.5

6. PUBLICATIONS RESULTING FROM AFOSR SPONSORED RESEARCH

1. "Chemiluminescence from the Gas Phase Reaction of Atomic Boron with the Alkali Metal Fluorides,": U.C. Sridharan, D.L. McFadden and P. Davidovits, J. Chem. Phys., 65, 5373 (1976).
   Also in ACS symposium Series No.56. P.R. Brooks and E.F. Hayes editors. p.136 American Chem. Soc. NY 1977.

2. "Production of Neutral Atoms by Pulsed Laser Heating," A. Prengel, J. DeHaven, E.J. Johnson and P. Davidovits, J. Appl. Phys., 48, 3551 (1977).

3. "Chemiluminescence from the Gas Phase Reactions of Atomic Carbon with PbO," U.C. Sridharan, T.G. DeGiuseppe, D.L. McFadden and P. Davidovits, Chem. Phys. Letters, 59, 43 (1978).

4. "Chemiluminescence Studies of Boron Atom Reactions with O_2 and N_2O", A. Brzychcy, J. DeHaven, A.T. Prengel and P. Davidovits, Chem. Phys. Letters, 60, 102 (1978).

5. "Rate Constants for the Reaction of Boron Atoms with O_2, SO_2, N_2O and CO_2," U.C. Sridharan, T.G. DiGiuseppe, D.L. McFadden and P. Davidovits, J. Chem. Phys., 70, 5422 (1979).

6. "Boron Atom Reactions II: Rate Constants with O_2, SO_2, CO_2 and N_2O," T.G. DiGiuseppe and P. Davidovits, J. Chem. Phys., 74, 3287 (1981).

7. "Studies of Chemiluminescence in Boron Atom Reactions with O_2, SO_2, N_2O and H_2O_2," James DeHaven, Michael T. O'Connor and P. Davidovits, J. Chem. Phys., 75, 1746 (1981).

8. "Studies of Chemiluminescence in Boron Atom Reactions with Epoxides," S.M. Hosseini, J. DeHaven and P. Davidovits, Chem. Phys. Letters, 86, 495 (1982).

9. "Boron Atom Reactions III: Rate Constants with H_2O, H_2O_2 and the Alcohols," T.G. DiGiuseppe, R.D. Estes and P. Davidovits, J. Phys. Chem, 86, 260 (1982).

10. "Boron Atom Reactions IV: Rate Constants with Epoxides," R. Estes, M.B. Tabacco, T.G. DiGiuseppe and P. Davidovits, Chem. Phys. Letters, 86 491 (1982).

11. "Boron Atom Reactions with the Epoxides: Vibrational Distributions in the product $BO(A^2\pi)$ state." M.K. Bullitt, P.R. Rao, J. DeHaven and P. Davidovits (in preparation).

12 "Boron Atom Reaction V: Rate Constants and Chemiluminescence Studies for the Second Series of Epoxides," M.B. Tabacco, C. Stanton and P. Davidovits (in preparation).

7. PERSONNEL

Degrees Awarded:

U.C. Sridharan,	Ph.D.	1978
A.M. Brzychcy	M.S.	1979
T.DiGiuseppe	Ph.D.	1980
R.D. Estes	M.S.	1981
S.M. Hosseini	M.S.	1981
J.J. DeHaven	Ph.D.	1982

Research Associates:

M. Bullitt
R. Rao

Current Graduate Students:

M.B. Tabacco
C. Stanton
J. Gardner

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